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(54) HEAT-RESISTANT SHEET COMPRISING LACTIC ACID POLYMER AND METHOD FOR PRODUCING MOLDER PRODUCT

(57)Abstract:

PURPOSE: To obtain the heat-resistant sheet improved in insufficient heat resistance which is the defect of the lactic acid polymer having excellent biodegradability, capable of being subjected to molding processes such as a vacuum-molding process, an air- pressure molding process and a vacuum and air-pressure molding process, and excellent in the release property from heated molds and in the mold duplicativity, and further to provide the method for producing the molded product suitable for general moldings produced from the sheet, especially food containers, blister-packaging materials, hot- filing containers, etc.

CONSTITUTION: The characteristics of the heat-resistant sheet having the lowest storage elastic modulus E' of 80-900kg/cm2 at a temperature lower by 20°C than the melting point by a test method relating to the temperature dependency of dynamic viscoelasticity comprises preliminarily crystallizing by the annealing of a sheet comprising a lactic acid polymer consisting mainly of polylactic acid and/or monoaxially or diaxially stretch-orienting the sheet. And the method for producing the recrystallized lactic acid molded product comprises molding the heat-resistant sheet in a heated mold within the range from a temperature lower by 20°C than the crystallization temperature Tc of the lactic acid polymer to a temperature below the melting point for 2-600sec.

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CLAIMS

[Claim(s)]
[Claim 1] The heat-resistant sheet which consists of a lactic-acid system polymer whose minimum value of the storage modulus (E') below temperature lower 20 degrees C than the melting point is 80-900kg/cm2 by the examining method (JIS-K- 7198 A law) about the temperature dependence of dynamic viscoelasticity characterized by the thing which are made to carry out preliminary crystallization or twists the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component on one shaft or two shafts by carrying out annealing processing, and to do for a stretch orientation.
[Claim 2] The heat-resistant sheet according to claim 1 which carries out annealing processing of the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component for - 600 seconds during 2 seconds at the temperature of under the melting point from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer, and is obtained by carrying out preliminary crystallization.
[Claim 3] The heat-resistant sheet according to claim 1 characterized by uniaxial stretching or carrying out biaxial stretching in the range it is 2 to 16 times whose field scale factor of this at the extension temperature of the range higher 50 degrees C than glass transition temperature (Tg) to the glass transition temperature (Tg) of a lactic-acid system polymer about the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component.
[Claim 4] The manufacture approach of the lactic-acid system mold goods characterized by making the heat-resistant sheet of any one publication of three recrystallize from claim 1 by fabricating with the metal mold heated for [for / 2 seconds / -] 600 seconds at the temperature of under the melting point from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Various shaping of a vacuum forming, pressure forming, vacuum pressure sky shaping, etc. is possible for this invention, and it relates to the manufacture approach of mold goods made from the heat-resistant sheet which was excellent in the mold-release characteristic in heating metal mold, and mold repeatability, and its sheet of having the thermal resistance which was especially suitable for food containers, such as a cup and a tray, the blister wrapping material, the hot philharmonic container, etc.
[0002]
[Description of the Prior Art] In recent years, plastics has caused serious terrestrial environmental problems, such as scene inhibition, a threat to a marine organism, and environmental pollution, with the trash, although the huge amount is used. Conventionally, as general-purpose resin used for a package, polyethylene, polypropylene, polystyrene, a polyvinyl chloride, polyethylene terephthalate, etc. are used, and incineration and reclamation are performed as the disposal approach of these resin.
[0003] However, there is a problem also in these disposal approaches, and since resin, such as polyethylene, polypropylene, and polystyrene, has the high combustion calorie, in incineration, it tends to damage a furnace and shortens the life of a furnace by it. Moreover, it is known that it will generate gas harmful at the time of incineration although the combustion calorie of a polyvinyl chloride is low. Also in reclamation, since these general-purpose resin has high chemical stability, remaining semipermanently, with the original form stopped is known, and it has become one of the causes which lack of reclaimed ground aggravates.
[0004] When discarded in natural environment, a fine sight is spoiled over a long period of time for the stability, and a marine organism, birds, etc. carry out an adding diet accidentally, and it has become the cause of environmental destruction, like a precious biomass is facing a crisis. In order to solve these problems, research of a biodegradability polymer is done briskly in recent years.
[0005] Polylactic acid and its copolymer are in one of the resin which attracts attention by the biodegradability polymer. Since the thing of a non-theory and the combustion calorie of biodegradability are low, this polymer has the description which does not damage a furnace and does not generate the still more harmful gas at the time of combustion, also when it destroys by fire. Moreover, since a refreshable biomass can be used for a start raw material, it can be freed from drained petroleum resources. From these things, it is expected as an alternative of general-purpose resin.
[0006] However, these polymers have thermal resistance as low as 50-degree-C order, the hot philharmonic container with which the thermal resistance of 80 degrees C or more used for a hood pack into which heating food is put, a daily dish container, a jam, and a pudding is demanded is difficult to use it for the field as which thermal resistance is required to some extent, and the service condition is limited from the heat-resistant problem also in other applications.
[0007] For example, also in transportation and storage of a sheet and mold goods, if it is in a transport container, a warehouse, etc. which are set in the sealing condition and temperature management of a

storage area is not performed, amounting to 50 degrees C or more on condition that summer etc. also has the problem it becomes impossible to use as a product according to generating of the welding between products, deformation, etc. with the conventional sheet and the mold goods of a lactic-acid system polymer not few.

[0008] Although it is shown in the U.S. Pat. No. 5,076,983 official report that heating contraction decreases from 66% to 4% by carrying out annealing of the 130 degrees C of the oriented films of polylactic acid for 1 minute, even if it performs pressure forming used for secondary forming of an extension sheet, on this condition, mold goods with good mold repeatability cannot be obtained. Moreover, by a sheet welding to metal mold, if annealing by metal mold is performed, the mold release from metal mold was difficult, and in order to prevent it, when thermal resistance was given to the sheet, there was a trouble that the mold repeatability of mold goods worsened.

[0009]

[Problem(s) to be Solved by the Invention] Therefore, the technical problem which this invention tends to solve improves the thermal resistance which is the fault of the lactic-acid system polymer which has the outstanding biodegradability, and shaping of a vacuum forming, pressure forming, vacuum pressure sky shaping, etc. is possible for it, and it is to offer the manufacture approach of the mold goods which are made from the heat-resistant sheet which was excellent in a heating metal mold mold-release characteristic and mold repeatability, and its sheet and which have the thermal resistance of general-purpose mold goods especially a food container, a blister wrapping material, a hot philharmonic container

[0010]

[Means for Solving the Problem] In order that this invention persons might solve an above-mentioned technical problem, various factors, such as molecular weight, were examined whenever [degree-of-crystallinity, crystallization rate, size / of a crystal /, and molecular orientation] as a factor which affects a moldability, but since these influence and suited mutually at the moldability, that it is difficult to discuss only by one factor became whether to be **.

[0011] For example, the welding to heating metal mold can be prevented by the approach of raising degree of crystallinity and raising thermal resistance. However, degree of crystallinity can be stopped low, even if it raises only the amount of preferred orientation, thermal resistance can go up, and the welding to metal mold can be prevented.

[0012] this invention persons are annealing, carrying out preliminary crystallization, and [0013] by holding for [2 seconds -] 600 seconds under with the melting point from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer, as a result of examining polylactic acid wholeheartedly as what covered the various above-mentioned factors on the macro paying attention to temperature distribution of the storage modulus (E') of dynamic viscoelasticity measurement of the sheet which consists of the lactic-acid system polymer used as a principal component. Or by raising thermal resistance and making the minimum value of the storage modulus (E') of a sheet into the range of 80-900kg/cm2 by performing the stretch orientation by one shaft and biaxial stretching It is made to recrystallize that raise thermal resistance to extent without the welding to metal mold, and a sheet with good mold repeatability is obtained at the time of shaping, and by fabricating with the metal mold heated further, finds out that the thermal resistance of mold goods may be raised, and came to complete this invention.

[0014] That is, this invention is a heat-resistant sheet which consists of a lactic-acid system polymer whose minimum value of the storage modulus (E') below temperature lower 20 degrees C than the melting point it is the examining method (JIS-K -7198, A law) about the temperature dependence of dynamic viscoelasticity characterized by the thing which are made to carry out preliminary crystallization or is depended on one shaft or two shafts, and to do for a stretch orientation, and is 80-900kg/cm2 by carrying out annealing processing of the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component

[0015] Moreover, this invention is a heat-resistant sheet obtained by being the temperature of under the melting point, carrying out annealing processing for - 600 seconds during 2 seconds, and carrying out

preliminary crystallization of the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component in detail from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer.
[0016] Furthermore, this invention is the extension temperature of the range higher 50 degrees C than glass transition temperature (Tg) to the glass transition temperature (Tg) of a lactic-acid system polymer about the sheet which consists of a lactic-acid system polymer which uses polylactic acid as a principal component, and is a heat-resistant sheet characterized by uniaxial stretching or carrying out biaxial stretching in the range it is 2 to 16 times whose field scale factor of this.
[0017] Moreover, this invention includes the manufacture approach of the lactic-acid system mold goods characterized by being the temperature under from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer to the melting point, and making an above-mentioned heat-resistant sheet recrystallize by fabricating with the metal mold heated for [for / 2 seconds / -] 600 seconds.
[0018] This invention is explained further below at a detail. Performing the examining method about the temperature dependence of the dynamic viscoelasticity in this invention by JIS-K -7198 and A law, the measuring range of 2 degrees C / min, and a storage modulus (E') went to temperature with the programming rate lower 20 degrees C than the melting point in that case. Moreover, glass transition temperature (Tg), crystallization temperature (Tc), and the melting point are Tig(s), Tpc(s), and Tpm(s) which are specified to JIS-K -7121, and programming rates are 10 degrees C / min.
[0019] Polylactic acid, its copolymer, etc. are raised as a lactic-acid system polymer which uses the polylactic acid of this invention as a principal component. As a manufacturing method of polylactic acid, the lactide which is an annular dimer is compounded from a lactic acid, and although many methods of obtaining the polylactic acid of the amount of macromolecules by ring opening polymerization are used, the approach of compounding polylactic acid by direct dehydration condensation from a lactic acid is also used.
[0020] The lactic acid used as a raw material is obtained by fermenting refreshable resources, such as sugar and starch. Moreover, it is compoundable also from a petrochemical raw material. The monomers of the raw material lactic acid used for this invention may be any of D object which is an optical isomer, L bodies, a meso object, and racemic modification, and may be such mixture. The ratio (ratio of length to diameter) of L in that case and D object can be used by all presentations to 100 / 0 - 0/100.
[0021] Moreover, as a copolymer of polylactic acid, the accessory constituent more than kinds, such as aliphatic series polyester, aromatic polyester, a caprolactone, vinyl acetate, an ethylene terephthalate polymer, and ethylene vinyl alcohol, is added immediately after the time of a polylactic acid polymerization, or a polylactic acid polymerization, and it is obtained by advancing a polymerization further.
[0022] The molecular weight of the lactic-acid system polymer used for this invention is the range of weight average molecular weight 50,000-700,000, and 70,000-300,000 are usually desirable from the point that reinforcement is highly excellent in fabrication nature especially.
[0023] Moreover, the heat-resistant sheet and mold goods of this invention may also contain additives other than a lactic-acid system polymer, such as other polymers, a plasticizer, a stabilizer, an anti-oxidant, an antiblocking agent, an antifogger, and a coloring agent, if needed. From after what has biodegradability ponders environmental protection as other polymers, it is desirable, for example, aliphatic series polyester, polyvinyl alcohol, polyhydroxy butyrate-hydroxy BARIRETO, a starch system polymer, etc. are mentioned.
[0024] Moreover, as an additive, unless the thermal resistance of the sheet of this invention and biodegradability are spoiled, it can use for this invention without a limit. For example, a stabilizer [carbodiimide / 1,3-butanediol, / plasticizers, such as polyester plasticizers, such as an adipic acid and a dioctyl phthalate, a polyethylene-glycol adipic acid, epoxidized soybean oil, a carbodiimide], 2, 6-Gee tertiary butyl-4-methyl phenol (BHT), [0025] Coloring agents, such as antifoggers, such as antiblocking agent [, such as anti-oxidants, such as a butylhydroxyanisol (BHA) a silica, and talc], glycerine fatty acid ester, and citric-acid mono-stearyl, titanium oxide, carbon black, and ultramarine blue, etc. may be

included.
[0026] Although the manufacture approach of a sheet performs fabrication by extrusion molding by T pressure die casting, a lactic-acid system polymer needs the moisture management in a production process, and since hygroscopicity is high and hydrolysis nature also has it, when carrying out extrusion molding using a common 1 shaft extruder, it needs to form it after moisture absorption and drying by a vacuum dryer etc. [high]
[0027] Moreover, it is also possible to perform multilayering according [since the dehydration effectiveness is high, efficient membrane formation is possible, and] to two or more extruders in membrane formation by the vent type twin screw extruder. In this case, it is possible to reinforce reinforcement by using the virgin layer which put in the recovery article in which physical properties are inferior to a main layer, and excelled [outer layers / both] in reinforcement.
[0028] Moreover, by putting a coloring agent only into a main layer, food etc. cannot be made to be able to touch a direct coloring agent component, it can also be made it, and it becomes possible by including a functional additive only in both outer layers further to acquire effective effectiveness by little addition.

[0029] Although especially the melting temperature at the time of carrying out sheeting of the lactic-acid system polymer is not restricted, it is temperature usually higher 10-50 degrees C than the melting point. The sheet by which melting extrusion was carried out is cast so that it may usually become predetermined thickness, and it is cooled by the need. In that case, when sheet thickness is thick, it considers as a uniform sheet by using electrostatic pinning properly, in being thin, a touch roll, the Ayr knife, and.
[0030] Although it is set to 0.2-3.0mm, if spacing of the lip which performs melting extrusion considers membrane formation nature, its 0.2-1.5mm will be desirable. Although not restricted especially about preliminary crystallization of the sheet obtained according to the above-mentioned process, the approach of carrying out fixed time amount contact etc. is mentioned on the approach of carrying out fixed time amount heating with radiant heat which carries out fixed time amount heating continuously with the air which carried out the forced convection in the tenter, such as an approach and an infrared heater, the heated hot platen, and a roll.
[0031] The approach of using especially a tenter is advantageous when performing industrial production. Although not limited about temperature and especially time amount, in order to obtain a proper crystallization rate, the annealing temperature of the sheet for performing preliminary crystallization is under the melting point from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer, and, as for annealing time amount, it is desirable to carry out 2 seconds or more.
[0032] the time of coincidence biaxial stretching after carrying out melting extrusion of the lactic-acid system polymer, making it the shape of a sheet as an approach of giving thermal resistance with a stretch orientation, and performing vertical extension processing or omitting this -- or let whenever [stoving temperature] serially be the range of temperature higher 50 degrees C than glass transition temperature (Tg) from glass transition temperature (Tg) at the time of horizontal extension of the inside at the time of biaxial stretching, or horizontal uniaxial stretching. The storage-modulus (E') range which needs a temperature requirement high 10-40 degrees C for the field condition of a sheet and a heat-resistant sheet is obtained, and it is especially especially more desirable than glass transition temperature (Tg).
[0033] In order to obtain sufficient storage-modulus (E') range, draw magnification is performed by uniaxial stretching or biaxial-stretching processing, and is obtained after that cooling below to glass transition temperature (Tg) immediately, or by performing annealing in the range of under the melting point from temperature lower 20 degrees C than the crystallization temperature (Tc) of a lactic-acid system polymer so that a field scale factor may serve as range which is two to 16 times. Especially, annealing temperature has especially the desirable range of temperature higher 40 degrees C than crystallization temperature (Tc) to it, in order to obtain a good field condition and good thermal resistance.
[0034] About sheet thickness, although the range of 50-1000 micrometers is desirable from the point of

the rigidity of mold goods, and the point of mold repeatability in the case where it uses for pressure forming, 100-500 micrometers is especially the most desirable from the point of practicality. Even when using for the possible vacuum forming of deep-drawing shaping, similarly, the range of 50-2000 micrometers is desirable, and especially 100-1000 micrometers are desirable from a practical point.
[0035] Although especially the orientation return stress of an extension sheet is not specified, it is desirable to use a 5-40kg/cm2 sheet by thickness conversion so that there may be no generating of the contraction at the time of shock resistance and shaping. In addition, orientation return stress is force which is going to restore to the condition before a sheet extending and is shown when the sheet for shaping which is measured based on ASTMD-1504, was extended and was obtained is heated, and it becomes the index which is called for as a value which broke the maximum stress by the cross section of a sheet, and shows molecular orientation extent of the extended sheet.
[0036] Next, the manufacture approach of mold goods is explained. The sheet for shaping of this invention is the vacuum forming and vacuum pressure sky shaping with which the non-extended thing used heating metal mold, and an extension sheet can obtain the mold goods of a predetermined configuration with pressure forming and vacuum pressure sky shaping which used heating metal mold.
[0037] Although especially a process condition is not restricted, as conditions in the case of using heating metal mold and a vacuum briquetting machine, its heating cycle time 5 - 60 seconds by the die temperature of 100-150 degrees C and metal mold are desirable at far-infrared heater temperature for 300-500 degrees C, and indirect heating time amount 5 to 30 seconds.
[0038] As conditions in the case of performing heating metal mold and a hot-platen pressure-forming machine, the compacting pressure of 1-10kg/cm2 is desirable for heating cycle time 1 to 20 seconds by the die temperature of 100-150 degrees C, and metal mold for heating time 0.5 to 6 seconds by the hot-platen temperature of 65-100 degrees C, and the hot platen. If it carries out on these conditions, the mold goods which the defect of the mold repeatability by underheat does not have generating of a lane drop, either, and were excellent in him can be obtained.
[0039] while the mold goods obtained by this invention have the biodegradability which is the description of a lactic-acid system polymer, a low combustion calorie, and the advantage which the harmful gas at the time of combustion does not generate, in the heat resistance test seen by 2% deformation of the molding at the time of leaving it for 10 minutes at predetermined temperature, to the thermal resistance of a lactic-acid system polymer container being 40 degrees C, it is markedly alike and, as for the container of this invention, the outstanding thermal resistance of 100 degrees C or more is shown. These general-purpose mold goods are widely used for hot philharmonic containers, such as a thing of a non-theory especially food and an object for a general package, for example, a pudding, a jam, and the Calais container, a food tray, a blister container, a clear case, etc.
[0040]
[Example] Although an example explains this invention further below at a detail, this invention is not limited to these from the first.
[0041] (Example 1 of reference) (the example of manufacture of a lactic-acid system polymer, P1)
the aliphatic series system polyester (50 mol % [of sebacic acids], propylene glycol 50 mol %) 5 weight section -- the L-lactide 85 weight section and the D-lactide 5 weight section -- in addition, after inert gas's having permuted the ambient atmosphere and mixing at 165 degrees C for 1 hour, the tin octanoate 0.02 section was added as an esterification catalyst, and the reaction was performed for 8 hours.
[0042] The obtained lactic-acid system polymer (P1 is called hereafter.) was transparent and colorless resin, and weight average molecular weight was 201,000 from the result of GPC. Moreover, glass transition temperature (Tg) was [107 degrees C and the melting point of 48 degrees C and crystallization temperature (Tc)] 156 degrees C.
[0043] (Example 2 of reference) (example of creation of a sheet)
The lactic-acid system polymer P1 was made into the absolute dry condition, on conditions with an extrusion temperature of 180 degrees C, it extruded with the extruder (the Tanabe plastics incorporated company make) of ratio-of-length-to-diameter=24 and 50mm of diameters of an extrusion screw, and

weight-average-molecular-weight 153,000, the thickness of 250 micrometers, and a 1000-micrometer sheet were obtained.

[0044] For the extrusion conditions of 250-micrometer sheet, screw-speed 24rpm and discharge quantity were [91kg/cm2 and the taking over rate of 16 kg/hr and back pressure] 3.6 m/min. For the extrusion conditions of 1000-micrometer sheet, screw-speed 45rpm and discharge quantity were [155kg/cm2 and the taking over rate of 25 kg/hr and back pressure] 1.2 m/min.

[0045] (Examples 1-5 and examples 1-5 of a comparison) The 250-micrometer lactic-acid system polymer (P1) sheet obtained by extrusion molding was inserted between two iron frames (bore of 20x20cm), and carried out fixed time amount annealing processing in the range for a maximum of 500 seconds into the oven controlled by 120 degrees C, and the sheet was produced.

[0046] Among these, the minimum value of a storage modulus (E') considered the thing of the range which is 80-900kg/cm2 as success, and checked the moldability. In addition, examples 4 and 5 experimented oven temperature as 100 degrees C and 135 degrees C respectively. Shaping performed the vacuum forming using the heating metal mold of 55mm long, the side of 122mm, a depth of 20mm, and a contraction ratio 0.36, and the same metal mold performed annealing processing for [120 degrees-C] 20 seconds succeedingly.

[0047] In addition, examples 1 and 3 experimented in the die temperature as 90,135 degrees C, respectively. While performing the storage modulus (E') and density measurement of a sheet which were obtained, the vacuum-forming condition was investigated. In addition, the storage modulus (E') measured the range of 0-100 degrees C on the frequency of 1Hz based on A law of JIS-K -7198, and calculated the minimum value. The consistency was measured based on the D method (measuring method with density gradient tubing) of JIS-K -7112.

[0048] Moreover, the three-stage estimated shaping condition evaluation of mold goods by the repeatability and the mold-release characteristic of a mold. It welded to metal mold completely, or there was no welding to x and metal mold about what mold repeatability is poor and was not able to fabricate, and although it was a configuration almost near metal mold, reappearance of a corner part made O what the welding to ** and metal mold does not have in a thing bad a little, either, and reproduced metal mold faithfully.

[0049] The thermal resistance of mold goods was put in into the oven of predetermined temperature, was left for 20 minutes, measured the length of a container, and the horizontal die length, and made them the temperature at the 2% contraction time from the rate of change. The obtained result is shown in Table 1.

[0050] The examples 1, 2, 3, 4, and 5 which are in within the limits whose minimum storage modulus (E') is 80-900kg/cm2 from a test result showed a good mold-release characteristic and mold reappearance. Although it depended also for the heat-resistant temperature of a cast on the die temperature, the good result 80 degrees C or more was obtained. Generally, although a consistency and degree of crystallinity have correlation, since a difference is in a moldability so that examples 1 and 2 and the examples 1 and 2 of a comparison may see also by the same consistency, it turns out only with degree of crystallinity that the shaping range cannot be specified.

[0051] (Example 6 of a comparison) It fabricated by making the die temperature of the example 1 of a comparison into ordinary temperature (21 degrees C).

[0052] (Example 7 of a comparison) It fabricated by making the die temperature of an example 1 into ordinary temperature (21 degrees C). Although the cast also with the good examples 6 and 7 of a comparison was obtained, the heat-resistant temperature of a cast became the low value of 50 degrees C or less.

[0053] (Examples 6-8 and example 8 of a comparison) The single-engined biaxial-stretching machine (the Iwamoto factory company make) performed 2x2 double extension for the 1000-micrometer lactic-acid system polymer (P1) sheet obtained by extrusion molding at predetermined temperature. While performing the amount of preferred orientation of the obtained sheet, a storage modulus (E'), and density measurement, the heat-resistant temperature in 2% contraction of a sheet was searched for.

[0054] Furthermore, using the same thing as the metal mold which used pressure forming of the above-

mentioned sheet in the example 1, annealing processing was performed similarly and the shaping condition was evaluated. The amount of preferred orientation was measured according to ASTMD-1504. The obtained result is shown in a table. The mold-release characteristic with good examples 6, 7, and 8 and mold reappearance included in within the limits whose minimum storage modulus (E') is 80-900kg/cm2 were shown. Each cast heatproof temperature also showed 100 degrees C and a high value. Moreover, it turns out in this case that the increment in a consistency is not accepted and cannot be specified with degree of crystallinity.

[0055] (Example 9 of a comparison) It fabricated by making the die temperature of an example 6 into ordinary temperature (21 degrees C). Cast heatproof temperature was 42 degrees C and a low value.

[0056] (Examples 9-13 and examples 10-14 of a comparison) The 1000-micrometer lactic-acid system polymer (P1) sheet obtained by extrusion molding was serially extended with the biaxial-stretching machine by the extension temperature of 65 degrees C, and 2x2 twice as many draw magnification as this. After the vertical extension with a roll, after horizontal extension was carried out in the extension zone of a tenter, as for the sheet obtained by extrusion, each temperature performed 10 and annealing for 20 or 30 seconds in the annealing zone controlled by 80,100,120 degrees C.

[0057] The obtained sheet searched for the heat-resistant temperature in 2% contraction of a sheet while performing a storage modulus (E') and density measurement. The minimum value of a storage modulus (E') considered the thing of the range which is 80-900kg/cm2 as success, and checked the moldability. Moreover, the example 10 of a comparison fabricated considering the die temperature of an example 11 as ordinary temperature (21 degrees C).

[0058] Moreover, the relation between storage-modulus E' (kg/cm2, axis of ordinate) obtained by dynamic viscoelasticity measurement and temperature (degree C, axis of abscissa) is shown in drawing 1 -3. The examples 9, 10, 11, 12, and 13 included in within the limits whose minimum storage modulus (E') is 80-900kg/cm2 showed a good mold-release characteristic and mold reappearance.

[0059] (Example 3 of reference) (the example of manufacture of a lactic-acid system polymer, P2) the aliphatic series system polyester (50 mol %, ethylene glycol 50 mol % and glass transition point, melting point of 105.0 degrees C) 5 weight section -- the L-lactide 85 weight section and the MESO-lactide 10 weight section -- in addition, inert gas permuted the ambient atmosphere, it mixed at 165 degrees C for 1 hour, and the 0.02 sections, in addition a 8-hour reaction were performed for tin octanoate as an esterification catalyst. [of succinic acids] [of -3.5 degrees C]

[0060] The obtained lactic-acid system polymer (the following P2 is called) was transparent resin which wore brown, and weight average molecular weight was 162,000 from the result of GPC. Moreover, glass transition temperature (Tg) was [104 degrees C and the melting point of 47 degrees C and crystallization temperature (Tc)] 148 degrees C.

[0061] (Example 4 of reference) (example of creation of a sheet)
When this lactic-acid system polymer (P2) was made into the absolute dry condition and it extruded with the same extruder as an example 1 on conditions with an extrusion temperature of 180 degrees C, weight-average-molecular-weight 131,000, the thickness of 250 micrometers, and a 1000-micrometer sheet were obtained.

[0062] For the extrusion conditions of 250-micrometer sheet, screw-speed 24rpm and discharge quantity were [89kg/cm2 and the taking over rate of 16 kg/hr and back pressure] 3.7 m/min. The extrusion conditions of 1000-micrometer sheet were [25kg / hr, and the back pressure of screw-speed 45rpm and discharge quantity] 149kg/cm2 and taking over rate 1.2 m/min.

[0063] (Examples 14 and 15) It evaluated by processing obtained 250-micrometer sheet by the same approach as an example 2. It evaluated by processing 1000 more micrometer sheet like an example 7. Consequently, good mold goods were able to be obtained. Moreover, heat-resistant temperature was also excellent with 100 degrees C or more.

[0064] (Example 5 of reference) (the example of manufacture of a lactic-acid system polymer, P3) Added the L-lactide 90 section, inert gas permuted the ambient atmosphere, the polyester (16 mol % and 14 mol [of isophthalic acid] % and 20 mol [of adipic acids] %, ethylene glycol 23 mol %, neopentyl glycol 27 mol %, number average molecular weight 23,800 (polystyrene conversion) of terephthalic

acids) 10 section containing aromatic carboxylic acid and aliphatic series dicarboxylic acid was made to do melting and mixing of both at 165 degrees C for 1 hour, and the 0.02 sections, in addition a 6-hour reaction were performed for tin octanoate in it as an esterification catalyst.
[0065] The copolymerization polymer (P3 is called hereafter.) of weight-average-molecular-weight 145,000 was obtained after reaction termination. The glass transition temperature (Tg) of this polymer was [(Tc) 108 degree C and the melting point of 49 degrees C and crystallization temperature] 157 degrees C.
[0066] (Example 6 of reference) (example of creation of a sheet)
When the lactic-acid system polymer (P3) was made into the absolute dry condition and it extruded with the same extruder as an example 1 on conditions with an extrusion temperature of 180 degrees C, weight-average-molecular-weight 121,000, the thickness of 250 micrometers, and a 1000-micrometer sheet were obtained.
[0067] For the extrusion conditions of 250-micrometer sheet, screw-speed 24rpm and discharge quantity were [90kg/cm2 and the taking over rate of 17 kg/hr and back pressure] 3.4 m/min. The extrusion conditions of 1000-micrometer sheet were [25kg / hr, and the back pressure of screw-speed 45rpm and discharge quantity] 151kg/cm2 and taking over rate 1.2 m/min.
[0068] (Examples 16 and 17) It evaluated by processing obtained 250-micrometer sheet by the same approach as an example 2. 1000 more micrometer sheet evaluated by performing the same processing as an example 7. Consequently, good mold goods were able to be obtained. Moreover, heat-resistant temperature was also excellent with 100 degrees C or more.
[0069] (Example 7 of reference) (example of creation of a sheet)
The 160-degree C press was performed for the weight molecular weight 230,000, glass-transition-temperature (Tg)50 degree C, and polylactic acid (the product made from PYURAKKU and the following P4 are called) with a melting point of 157 degrees C by the absolute dry condition, and the sheet (250 micrometers and 1000 micrometers) was obtained.
[0070] (Examples 18 and 19) It evaluated by processing 250-micrometer sheet obtained in the example 7 of reference by the same approach as an example 2. 1000-micrometer sheet also evaluated by performing the same processing as an example 7. Consequently, good mold goods were able to be obtained. Moreover, heat-resistant temperature was also excellent with 100 degrees C or more.
[0071]
[Table 1]

（表1）未延伸アニーリング処理

未延伸 ｱﾆｰﾘﾝｸﾞ処理	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
ｱﾆｰﾘﾝｸﾞ温度[℃]	１２０	１２０	１２０	１００	１３５
処理時間[sec]	４５	６０	９０	５００	◠３０
最小貯蔵弾性率 [Kg/cm²]	１００	３００	８５０	４００	２００
密度 [g/cm³]	1.249	1.249	1.254	1.251	1.250
金型成形温度[℃]	９０	１２０	１３５	１２０	１２０
成形状態	○	○	○	○	○
成形品耐熱温度 [℃]	８５	１１０	１２０	１００	１１０

[0072]
[Table 2]
（表2）未延伸アニーリング処理

未延伸 ｱﾆｰﾘﾝｸﾞ処理	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
ｱﾆｰﾘﾝｸﾞ温度[℃]	１２０	１２０	１２０	１２０	１２０
処理時間 [sec]	無	３０	１２０	１８０	６００
最小貯蔵弾性率 [Kg/cm²]	４０	５０	１１００	１１５０	２０００
密度 [g/cm³]	1.249	1.249	1.255	1.257	1.264
金型成形温度[℃]	１２０	１２０	１２０	１２０	１２０
成形状態	×	×	△	△	×
成形品耐熱温度	－	－	－	－	－

[0073]
[Table 3]

(表3) 未延伸アニーリング処理

未延伸 ｱﾆｰﾘﾝｸﾞ処理	比較例 6	比較例 7	実施例 14	実施例 16	実施例 18
ｱﾆｰﾘﾝｸﾞ温度[℃]	120	120	120	120	120
処理時間 [sec]	無	60	60	60	60
最小貯蔵弾性率 [Kg/cm²]	40	300	250	300	350
密度 [g/cm³]	1.249	1.249	1.249	1.250	1.249
金型成形温度[℃]	21	21	120	120	120
成形状態	○	○	○	○	○
成形品耐熱温度 [℃]	42	50	110	110	110

[0074]
[Table 4]
(表4) 延伸処理のみ

延伸処理のみ	実施例 6	実施例 7	実施例 8	比較例 8	比較例 9
延伸温度[℃]	60	65	70	80	60
配向度 MD [Kg/cm²] CD	25 28	15 19	6.4 8.0	2.8 4.2	25 28
最小貯蔵弾性率 [Kg/cm²]	700	600	200	30	700
密度 [g/cm³]	1.250	1.249	1.250	1.250	1.250
金型成形温度 [℃]	120	120	120	120	30
成形状態	○	○	○	×	○
成形品耐熱温度 [℃]	100	100	100	−	42

[0075]

[Table 5]
（表５）延伸後アニーリング処理（アニーリング温度８０℃）

延伸後ｱﾆｰﾘﾝｸﾞ処理 (ｱﾆｰﾘﾝｸﾞ温度80℃)	実施例 9	実施例 １０	実施例 １１	比較例 １０
処理時間 [sec]	１０	２０	３０	３０
最小貯蔵弾性率 [Kg/cm²]	９０	１２０	１２０	１２０
密度 [g/cm³]	1.249	1.249	1.249	1.249
シート耐熱温度[℃]	４２	４４	４５	４５
金型成形温度[℃]	１２０	１２０	１２０	２１
成形状態	○	○	○	○
成形品耐熱温度[℃]	１００	１００	１１０	４２

[0076]
[Table 6]
（表６）延伸後アニーリング処理（アニーリング温度１００℃）

延伸後ｱﾆｰﾘﾝｸﾞ処理 (ｱﾆｰﾘﾝｸﾞ温度100℃)	実施例 １２	実施例 １３	比較例 １１
処理時間 [sec]	１０	２０	３０
最小貯蔵弾性率 [Kg/cm²]	１３５	８００	１０５０
密度 [g/cm³]	1.245	1.250	1.252
シート耐熱温度 [℃]	４５	８０	１００
金型成形温度 [℃]	１２０	１２０	１２０
成形状態	○	○	△
成形品耐熱温度[℃]	１００	１００	１１０

[0077]
[Table 7]

（表7）延伸後アニーリング処理（アニーリング温度１２０℃）

延伸後ｱﾆｰﾘﾝｸﾞ処理 (ｱﾆｰﾘﾝｸﾞ温度120℃)	比較例 １２	比較例 １３	比較例 １４
処理時間［sec］	１０	２０	３０
最小貯蔵弾性率 ［Kg/cm²］	１０５０	１１００	１１５０
密度［g/cm³］	1.256	1.257	1.258
シート耐熱温度［℃］	６０	９０	１２０
金型成形温度［℃］	１２０	１２０	１２０
成形状態	△	△	△
成形品耐熱温度［℃］	１００	１００	１１０

[0078]
[Table 8]
（表８）延伸処理のみ

延伸処理のみ	実施例 １５	実施例 １７	実施例 １９
延伸温度［℃］	６５	６５	６５
配向度 MD ［Kg/cm²］ CD	１４ １７	１６ ２１	２０ ２４
最小貯蔵弾性率 ［Kg/cm²］	５５０	６３０	６８０
密度［g/cm³］	1.249	1.250	1.249
金型成形温度 ［℃］	１２０	１２０	１２０
成形状態	○	○	○
成形品耐熱温度 ［℃］	１００	１００	１１０

[0079]
[Effect of the Invention] This invention improves the thermal resistance which is the fault of the lactic-

acid system polymer which has the outstanding biodegradability, and can offer the manufacture approach of mold goods of having the general-purpose mold goods made from the heat-resistant sheet which was excellent in the heating metal mold mold-release characteristic which can fabricate a vacuum forming, pressure forming, vacuum pressure sky shaping, etc., and mold repeatability, and its sheet, and the outstanding thermal resistance which was suitable for the food container, the blister wrapping material, the hot philharmonic container, etc. especially.

[Translation done.]